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Technical Report No. 4

to the

Office of Naval Research
and
Advanced Research Projects Agency
ARPA Order No. 299, Amend. 6
Contract Nonr 4511(00)
Task NR 356-464

CHEMILUMINESCENT SYSTEMS

MONSANTO RESEARCH CORPORATION
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ABSTRACT

Another functional class of organic materials, electronegatively substituted vinyl compounds, have been observed to yield relatively bright chemiluminescence in autoxidation reactions in basic, aprotic polar solvents. 4-Dimethyl amino benzoin has been found to produce a peak emission intensity significantly greater than that of benzoin. The relative emission intensities of indoles are orders of magnitude greater in aprotic solvents than in aqueous solution. For 2,3-dimethylindole this ratio is $>10^6$.

Luminescence spectra have been obtained for benzoin, 2,3-dimethylindole and indole-5-carboxylic acid as a function of degree of reaction and base concentration. The observed chemiluminescence spectrum for benzoin oxidation corresponds to the fluorescence spectrum of benzil although benzil fluorescence has not been observed in the luminescence spectrum of oxidized benzoin solutions. The chemiluminescence spectrum of 2,3-dimethylindole corresponds to the fluorescence spectrum of a stable reaction product. The chemiluminescence spectrum of indole-5-carboxylic acid is similar to that of 2,3-dimethylindole but does not correspond with the fluorescence spectrum of any observed (stable) product.

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I. INTRODUCTION

The objective of this research program is the discovery of bright chemiluminescent reactions suitable for development into practical field systems. The approach adopted has been to select relatively simple classes of organic compounds, suggested by structural analogy to known chemiluminescent compounds, and to determine the gross brightness of their autoxidation reactions in strongly basic solution in aprotic, polar solvents (ref. 1). In this manner a number of new classes of relatively bright chemiluminescent reactions have been identified.

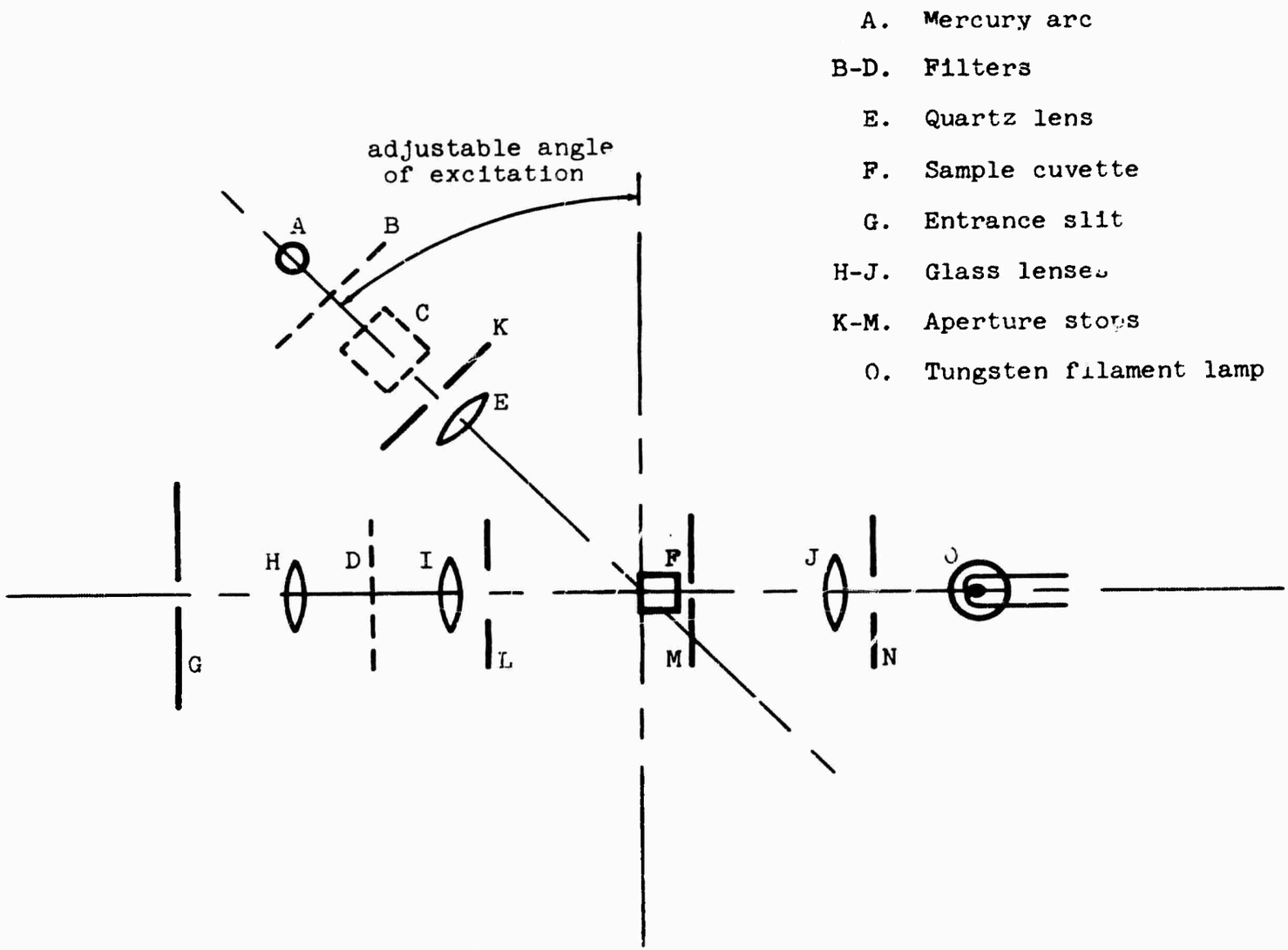
In this report we present additional results of this survey (ref. 2) with emphasis on acyloins, indoles, polynuclear aromatic compounds, and electronegatively substituted vinyl compounds. For the acyloins and indoles the gross brightness has been determined for a series of structurally related compounds.

Detailed studies have been initiated for selected indoles and acyloins by determination of important reaction parameters and luminescence spectra.

II. INSTRUMENTATION

A double optical bench has been added to the scanning monochromator to permit determination of fluorescence, chemiluminescence, and absorption spectra on a single sample (Figure 1). The excitation wavelength band is selected by a suitable filter combination. Both front surface and right angle excitation may be obtained by rotation of the excitation bench.

A calibrated Eppley Bi-Ag linear thermopile has been received for determination of the relative spectral response of our photomultipliers.



A. Mercury arc
B-D. Filters
E. Quartz lens
F. Sample cuvette
G. Entrance slit
H-J. Glass lenses
K-M. Aperture stops
O. Tungsten filament lamp

Figure 1. Schematic Diagram of Optical Bench for Fluorescence, Chemiluminescence and Absorption Measurements

III. EXPERIMENTAL RESULTS

A. SURVEY OF LUMINESCENCE IN AUTOXIDATIVE CHEMILUMINESCENT REACTIONS

1. Introduction

In Appendix I we present a complete tabulation of the chemiluminescence of all compounds surveyed in the past quarter. Reactions for which the gross brightness exceeds one per cent of a standard tritiated phosphor source are arbitrarily considered to be "bright". The bright reactions are further divided into "true" autoxidations and "initial flash" reactions.

This second category of "bright" chemiluminescent reactions are those that produce an initial flash decaying with an observed half-life of the order of 2-3 seconds and that are insensitive to oxygen in the sense that the initial peak intensity is not again achieved after oxygen addition. In this class the effective reactants are generally unknown and are not further considered here.

Autoxidation reactions are taken to be those with induction periods and/or decay half-lives longer than those calculated for stoichiometric reaction at the known oxygen introduction rate. The standard reactant concentration of 5×10^{-3}M was selected to be large compared to the dissolved oxygen concentration of the air-saturated solutions, namely, 7×10^{-4}M (in O_2) for pure dimethylsulfoxide (DMSO) and 1.1×10^{-3} for pure dimethylformamide (DMF), both at 20°C (ref. 4). The standard oxygen addition rate is equivalent to 5×10^{-4} mole O_2/liter-sec. Thus, for oxygen-limited reactions one expects that after the initial mixing reaction, an induction period of 1-2 seconds will be necessary to establish the steady state oxygen concentration and the peak emission intensity. This should be followed by decay with a half-life exceeding five seconds if the expected autoxidation reaction is taking place. The above definition has the practical advantage that reactions involving low concentrations of impurities are effectively excluded. Of course, autoxidations that are rapidly quenched by reaction products will also be excluded.

2. Indoles

a. Relative Brightness in DMSO

The peak brightness ratios and decay half-lives determined for indoles are given in Table 1. The "figure-of-merit" is the product of these two quantities and is roughly proportional to the integrated emission from the reaction (ref. 1). The brightest emission has been observed for skatole (3-methylindole) and 2,3-dimethylindole. The brightness of the latter compound is surprising since Philbrook reported 2,3-dimethylindole to be inactive in chemiluminescence in aqueous, alkaline persulfate (ref. 3).

Table 1

CHEMILUMINESCENCE OF THE INDOLES

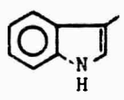
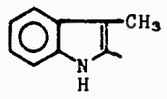
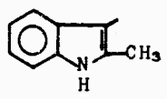
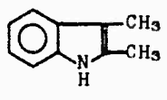
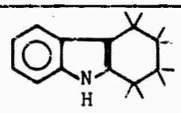
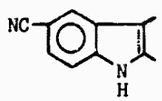
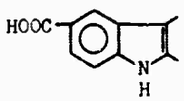
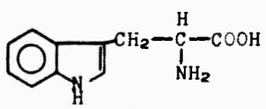
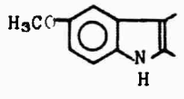
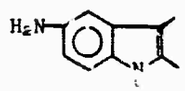
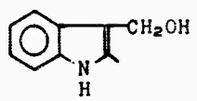
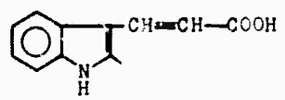
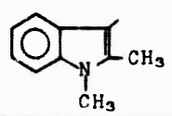
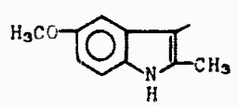
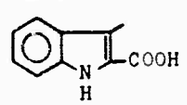
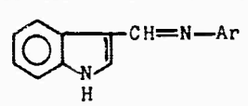
Compound	Structure	100 I/Io	$t_{1/2}$†	"Figure of Merit" 100 I/Io x $t_{1/2}$ (sec)
Indole		30	250 s	7.5×10^3
Skatole		6×10^3	290 s	1.74×10^6
2-Methylindole		6	54 s	3.2×10^2
2,3-Dimethylindole		6×10^3	60 s	3.6×10^5
1,2,3,4-Tetrahydrocarbazole		2.6	50 s	1.3×10^2
5-Cyanoindole		2.6	9 h	8.4×10^4
Indole-5-carboxylic acid		110	3500 s	3.8×10^5
L-Tryptophan		86	483 s	4.4×10^4
5-Methoxyindole		1.3	120 s	1.5×10^2

Table 1 (Continued)

Compound	Structure	100 I/Io	$t_{1/2}$†	"Figure of Merit" 100 I/Io x $t_{1/2}$ (sec)
5-Aminoindole		1.1	13 s	1.43×10^1
Indole-3-carbinol		8.6	9 m	4.6×10^3
3-Indoleacrylic acid		1.1	16 m	1.05×10^3
1,2-Dimethylindole		1.2	270 s	3.24×10^2
5-Methoxy-2-methylindole		1.0	6 m	3.6×10^2
Indole-2-carboxylic acid		0.5	5 m	1.5×10^2
3(N-Arformimidoyl)indoles		≤1*	small	—

* See previous report for details.

Conditions: 0.1M K^+tBuO^- in DMSO + O_2.
Conc. of compound - 5×10^{-3}M

† Abbreviations: s - seconds
m - minutes
h - hours

The "figure-of-merit" for 2,3-dimethylindole is reduced five-fold compared to skatole as a result of the shorter half-life of the reaction.

b. Comparison of Relative Brightness in DMSO and in Water

A comparison of the relative brightness of the indoles in aqueous persulfate as reported by Philbrook et al, (ref. 3) to that of the same compounds in DMSO-potassium t-butoxide (t-BuOK) is given in Table 2. Note that the brightest compound in each system has been normalized to 100 (Columns 1 and 2). We estimate from Philbrook's values for his weakest emittor, indole-3-acetic acid, that the sensitivity limit in his apparatus is ≈4 on a scale where indole-5-carboxylic acid equals 100. Comparison of the two scales of Table 2 indicates that a far greater range of intensities is observed in the t-BuOK-DMSO system. The relative brightness of the two scales has been roughly established by determination of the relative brightness of skatole in our photometers in alkaline aqueous persulfate*

We found a brightness ratio of 10^5 for skatole in the two systems; i.e., 100 on our scale represents an emission intensity of $59/100 \times 10^5 \approx 6 \times 10^4$ greater than 100 on Philbrook's scale**. It is, therefore, not at all surprising to find a much greater range of brightness for the chemiluminescence of the indoles in DMSO. The relative brightness ratios for the same compounds in the two reaction media (Column 3 of Table 2) are seen to range from a minimum 300-fold increase for 2-methylindole to $>10^6$ for 2,3-dimethylindole. A possible explanation for this phenomenon may be the much greater base strength in the DMSO-t-BuOK solution, permitting ionization of weaker acids and avoiding the leveling expected with weak bases.

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* In attempting to reproduce Philbrook's results for indole-5-carboxylic acid in aqueous solution, we did not observe the induction period reported for attainment of maximum luminescence, although this was seen with skatole. The chemiluminescence intensity of the 5-carboxylic acid was found to be an order of magnitude less than that for skatole, in disagreement with Philbrook's results. Comparison was thus made for the more favorable, brighter species. A possible explanation for this disagreement was that our reactant concentration was two-fold greater. Confirming Philbrook's observations, no measurable emission was found for 2,3-dimethylindole in aqueous solution.

** These rough comparisons take no account of possible spectral shifts.

Table 2

COMPARISON OF RELATIVE BRIGHTNESS FOR INDOLES IN AQUEOUS AND DMSO SOLUTIONS*

Conditions:

OH^- - 0.5M
$S_2O_8^=$ - 0.08M
K^+tBuO^- - 0.1M
Conc. of reactants - 5×10^{-3}M

Compound	Normalized Intensity Aqueous Alkaline Persulfate, O_2	Normalized Intensity DMSO, K^+tBuO^-, O_2	Relative Intensity DMSO/Aqueous
Indole-5-carboxylic acid	100	1.8	10^3
3-Methylindole	59	100	10^5
2,3-Dimethylindole	0 (<4)	100	1.5×10^6
Indole	44	0.50	7×10^2
1,2-Dimethylindole	41	0.020	3×10^2
2-Methylindole	30	0.10	2×10^3
L-Tryptophan	18	2.1	7×10^4

* See text.

c. Relative Brightness vs Structure

In DMSO 5-cyanoindole and indole-5-carboxylic acid stand out as compounds of large "figure-of-merit" in spite of low relative brightness as a result of their long decay half-lives. The decay half-life of ≈9 hours of 5-cyanoindole is the greatest we have observed. It is of interest that the 5-substituted electron withdrawing indoles are much more efficient than indole, whereas the 5-substituted electron donating indoles (5-methoxy, 5-amino) are both far less efficient than indole. The observed "figures-of-merit" correlate with Hammett's σ values (ref. 5), with efficiency decreasing in the order CN > H (indole) > OCH_3 > NH_2. The 5-carboxylate does not fit this correlation well, perhaps as a result of the formation of the doubly charged indole dianion.

Another striking comparison is the brightness decrease of three orders of magnitude observed between 2,3-dimethylindole and the related cycloalkane 1,2,3,4 tetrahydrocarbazole. Replacement of the cycloalkane ring by another aromatic nucleus (carbazole) decreases the brightness further, but by only one order of magnitude.

Substitution on the methyl group of skatole demonstrates the same high structure sensitivity. Thus, the 3-(N-aryl formimidoyl) indoles, which may be taken as aldehyde precursors, are very weak emittors. As the perturbation of the methyl group is decreased we find increasing intensity in the order 3-indole acrylic acid < indole 3-carbinol < L-tryptophan. The latter, a substituted 3-ethylindole, is considerably more efficient than indole.

d. Relative Brightness vs Concentration

The dependence of the peak emission intensity of the chemiluminescence of skatole in DMF upon concentration has been investigated. The results are presented in Figure 2 and compared to the results previously reported for DMSO (ref. 1). At low concentrations the DMF peak intensities are considerably greater than those in DMSO. The ratio appears to be increasing with concentration until quenching occurs. The maximum brightness of the two systems is the same, indicating that the excited state concentration is the controlling reaction parameter. The "figure-of-merit" of 5 x 10^{-3}M skatole in DMF is about three-fold greater than in DMSO.

3. Acyloins

a. Relative Brightness vs Structure

Data on the chemiluminescence of the acyloins obtained to date are summarized in Table 3. A substituted benzoin, 4-dimethylaminobenzoin, has been found that is significantly brighter than benzoin. Two derivatives of 4,4'-dihydroxybenzoin become even

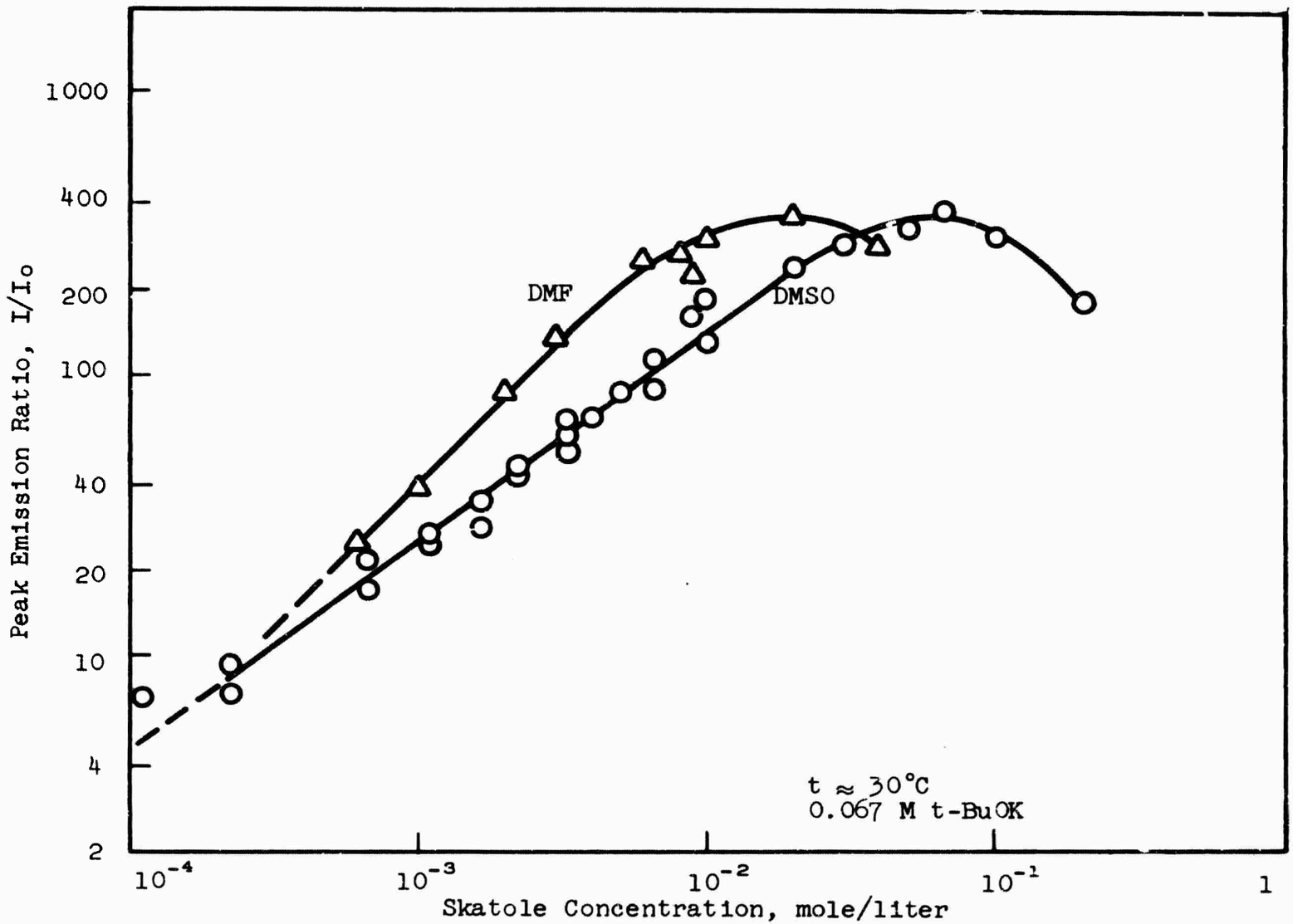


Figure 2. Peak Emission Intensity for Skatole Autoxidation in DMSO and DMF as a Function of Skatole Concentration

Table 3

CHEMILUMINESCENCE OF ACYLOINS

Reaction Conditions:

5×10^{-3}M in DMSO
t-BuOK 0.1M
O_2 flow rate ≈0.3 cm^3/sec
sample volume 30 cm^3
cross section 2.5 cm
fritted gas dispersor

Compound	Initial Pulse 100 I/I_o	Time to Peak*	Peak Intensity, 100 I/I_o	$t_{1/2}$*	Remarks
4-Dimethylaminobenzoin	0.2	23 s	40.0	8 s	Same color sequence as benzoin
Benzoin	0.1	14 s	15	8 s	
Anisoin	0.1	22 s	6.5	7 s	
4,4'-Dihydroxybenzoin	0.24	30 s	2.4	60 s	colorless solution
2,2'-Dihydroxybenzoin	1.8	18 s	0.45	18 s	
		3 m	0.22	2.8m	second peak
Furoin	0.8	5 m	0.3	7 s	capillary bubbler
Acetoin	0.24	45 s	0.12	-	
		5 m	0.13	5 m	second peak
4,4'-Dihydroxy-3,3'-dimethoxybenzoin	6.0	5 s	0.34	5 m	colorless solution
3,3'-Dichloro-4,4'-dihydroxybenzoin	3.0	5 s	0.50	25 s	colorless solution
L-Ascorbic acid	0.6	30 s	0.36	15 s	colorless solution
Blank	0.2	20 m	0.02	long	

* s = seconds, m = minutes

weak emittors as a result of further substitution. Like the parent compound, they also do not display the intense absorption characteristic of the radical anion. This phenomenon is probably explained on the basis of unhindered quinone formation for the 4,4'-compounds compared to the hindered 2,2'-dihydroxybenzoin, which appears to react through the normal radical anion. Since the emission intensity is not corrected for self-absorption, the relative values for the 4,4'-dihydroxybenzoins cannot be directly compared to values for the acyloin series.

b. Absorption Spectra

The ultraviolet absorption spectrum of air-free 5×10^{-4}M benzoin and 1×10^{-2}M $K^+t\text{-}BuO^-$ in DMSO displays two absorption peaks (above the DMSO cutoff at 270 mμ), one at 360 mμ and the other at 330 mμ. As air is added to the alkaline solution of benzoin, the 330 mμ peak gradually disappears and the 360 mμ peak broadens considerably (with a large decrease in the optical density). The addition of more air to the solution resulted in the discharge of the light green color. The absorption spectrum of this colorless solution is featureless to the cutoff (OD = 2) at about 300 mμ. The original benzoin-base solution cutoff is at 280 mμ.

4. Vinyl Compounds

Vinyl compounds containing electronegative substituents have been found to undergo autoxidation with the emission of "bright" chemiluminescence. The pertinent data are summarized in Table 4 for these compounds and some related weaker emittors.

Acrolein, $H(CH{=}CHCHO)$, crotonaldehyde, $CH_3(CH{=}CHCHO)$, and cinnamaldehyde, $\phi(CH{=}CHCHO)$ yield relative emission intensities of 200, 66, 1, respectively. The effect of the substitution may perhaps be correlated with the size of the substituents. Substitution of groups adjacent to the olefinic linkage in methyl vinyl ketone produces similar trends. The phenyl derivative, in this case, diminishes the intensity to a tenth of that observed for the parent compound.

Replacement of the vinyl group with methyl (giving the compound acetone) essentially eliminates chemiluminescence. An unsaturated analogue of acetone that is heavily substituted, dianisidene acetone, has a chemiluminescent intensity similar to that of acetone.

The carboxylate anion does not appear to be effective in promoting chemiluminescence; for example, there is no significant difference in the luminescence of the saturated and unsaturated dibasic compounds: succinic and maleic or fumaric acids.

Table 4

CHEMILUMINESCENCE OF VINYL COMPOUNDS

Conditions:

0.1M K^+tBuO^- in DMSO + O_2
conc. reactant - 5×10^{-3}M

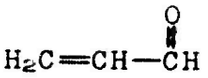
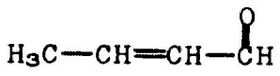
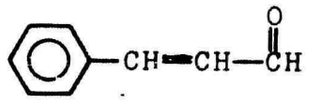
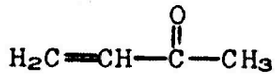
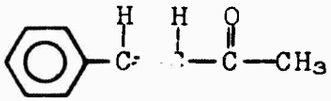
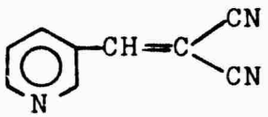
Compound	Structure	Initial Pulse 100 I/Io	Peak Intensity, 100 I/Io	$t_{1/2}$†	Remarks
Acrolein (stabilized with hydroquinone at 100 ppm)		8.0	7.0	11 s	lt red after reaction
Crotonaldehyde		2.6	2.7	6 s	dk red after reaction
Cinnamaldehyde		15.0	4×10^{-2}	—	lt red after reaction
Methyl vinyl ketone		2.4	8.2	21 s	dk red after reaction

Table 4 (Continued)

Compound	Structure	Initial Pulse 100 I/Io	Peak Intensity, 100 I/Io	$t_{1/2}$ +	Remarks
Trans-4-phenyl-3-buten-2-one		0.8	0.8	17 s	lt red after reaction
Acrylonitrile	$CH_2{=}CH{-}CN$	0.1	1.2	75 s	dk red after reaction
Crotonitrile	$CH_3{-}CH{=}CH{-}CN$	2.6	2.7	45 s	dk red after reaction
3-Pyridylmethylene-malonitrile		0.64	3.6	4 m	--

+ s = seconds
m = minutes

Although the data on this class of chemiluminescent reactions are still fragmentary, they are of interest, first, because of the molecular simplicity of the reactants and second, because of their possible relationship to the luminescence of the ethylene derivative tetrakis dimethylamino ethylene (TMAE).

5. Polynuclear Aromatic Hydrocarbons

The chemiluminescence of fluorene and fluoranthene appears to be related to that of the acyloins by ketyl formation and oxidation. Preliminary results indicate a decrease in the chemiluminescence intensity in the following order: 9-hydroxyfluorene > fluorene > 9-fluorenone. The results for 9-fluorenone may perhaps be reconciled on the assumption that the material contained a reducing impurity, i.e., fluorene or fluorenone.

Acridine, one of the brightest compounds investigated, is intriguing because of its similarity to lucigenin. As in the case of fluorenone, we speculate that the acridine may contain a reducing impurity, such as acridan. Russel, et al, (ref. 6) have shown that radical anions are formed in high yield by electron transfer from such couples, i.e., fluorene-fluorenol, acridine-acridan, etc. Chemiluminescence associated with ketyl oxidation has been reported by Chandross (ref. 7).

B. LUMINESCENCE SPECTRA

1. Indoles

The chemiluminescence spectra of indole-5 carboxylic acid and 2,3-dimethylindole are shown in Figure 3, curve B, and Figure 4, curve B, respectively.

The chemiluminescence emission of 2,3-dimethylindole peaks at 512 mμ. This band should be compared with the luminescence spectrum of the indole in base-free, air-free solution (Figure 4, curve A), and to indole in the presence of base (Figure 4, curve C). The emission intensity of this indole is attenuated in alkaline solutions and is accompanied by a 50 mμ shift to the red. The absence of any 360-370 mμ emission peaks in the base-indole solution suggests that the indole is completely converted to the anion.

The emission spectrum of the autoxidation-induced chemiluminescence does not correspond to the fluorescence emission of either the indole or its anion. Small quantities of air were injected into the base-indole solution; the luminescence spectra of the partially oxidized solutions so obtained are given in curves D-F. (The quantity of air does not correspond to the quantity of oxygen dissolved or reacted but is related to the fraction of indole reacted.) The red peak at 506 mμ formed after 22 ml of air was injected (curve F) corresponds very closely to the chemiluminescence

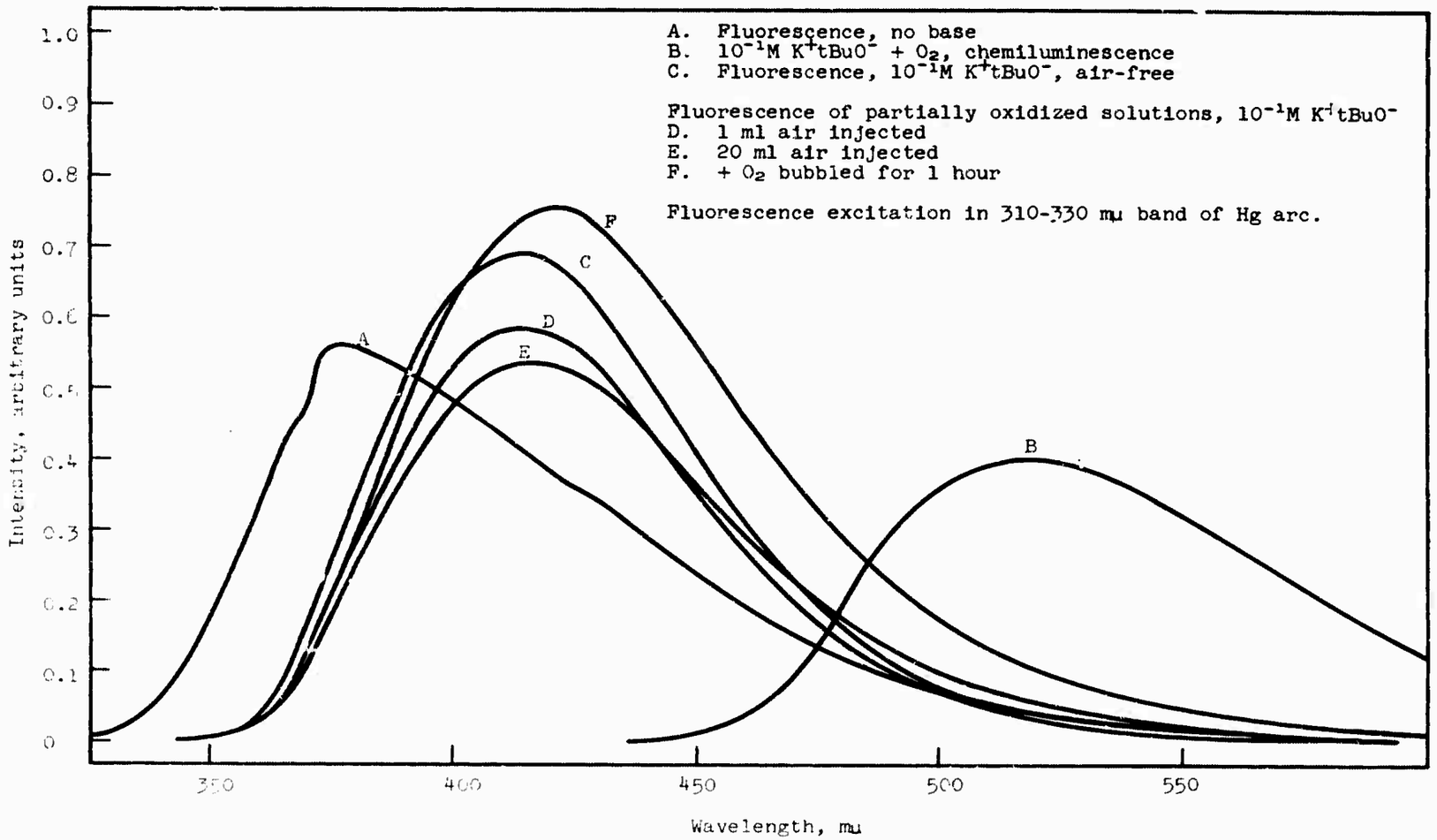


Figure 3. Fluorescence and Chemiluminescence Spectra of Indole-5-Carboxylic Acid, 5 x 10^{-3}M in DMSO

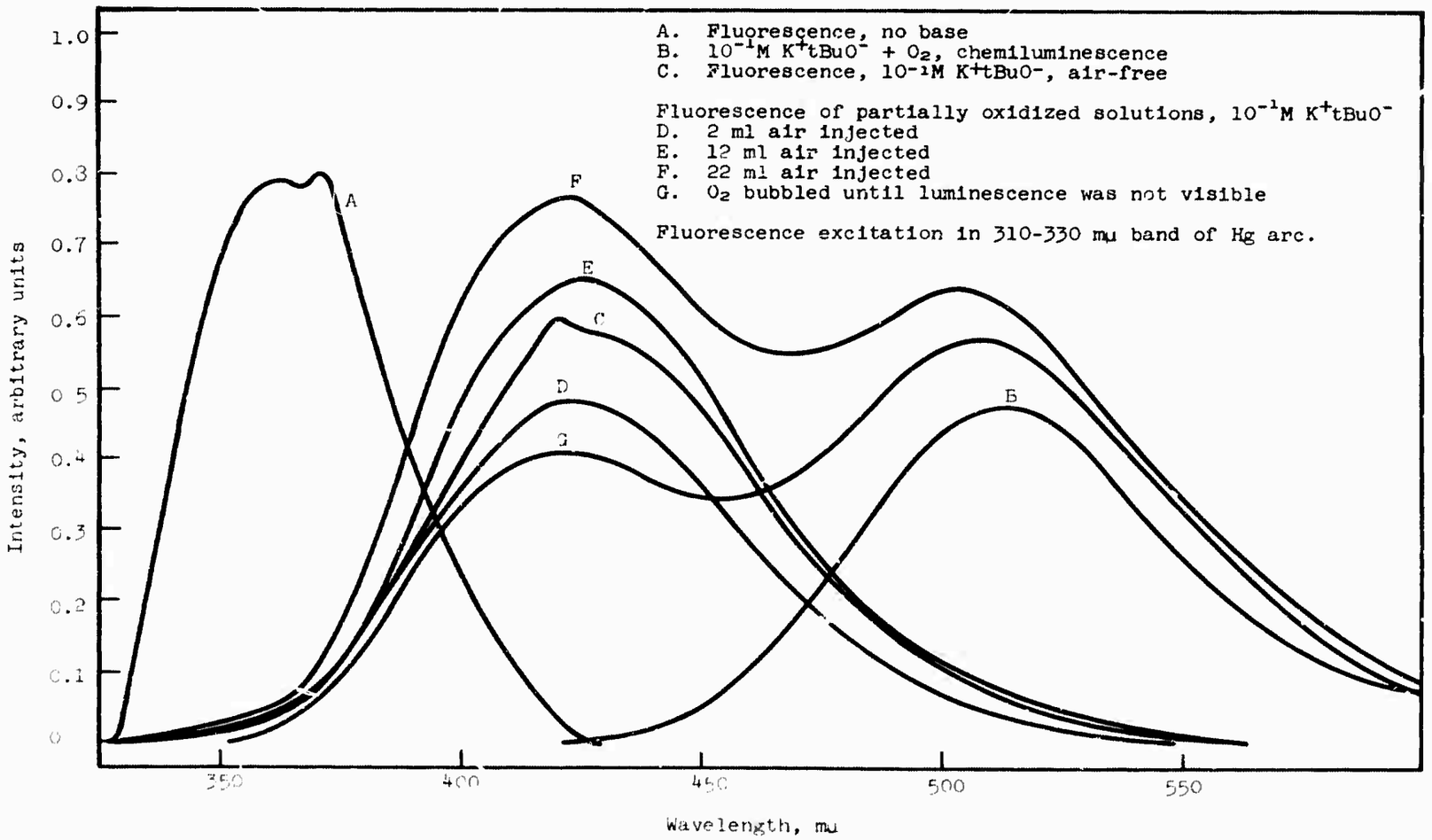
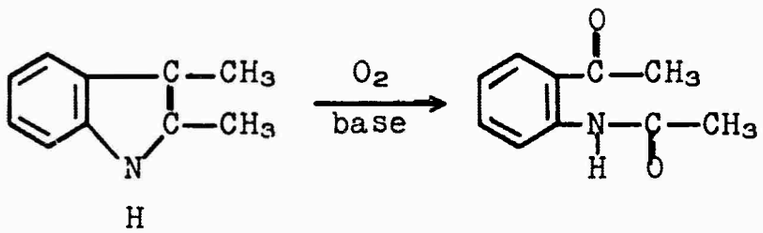


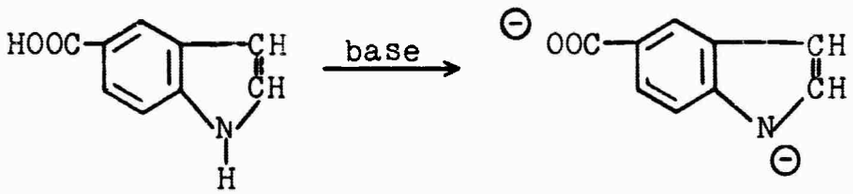
Figure 4. Fluorescence and Chemiluminescence Spectra of 2,3-Dimethylindole, 5×10^{-3}M in DMSO

peak. The 422 mμ band was assumed to be the anion fluorescence, and this band, curve C, was subtracted from the fluorescence spectrum of the oxidized solution, curve G. The red peak was found to resemble closely the chemiluminescence emission. This very close identity of the two spectra suggests that the emittor is a stable species.

The measurements of the total chemiluminescence emission intensity indicated that the peak intensity of luminescence was obtained within a short period of time following injection of oxygen. This suggests that the emittor forms in the initial stages of the decomposition. A major product would be expected to be that formed through the cleavage of the heterocyclic ring double bond to the diketone, namely:



The fluorescence spectrum of indole-5 carboxylic acid is given in curve A, Figure 3. The indole anion(s) formed in 0.1M t-butoxide has an emission spectrum (curve B) shifted toward the red as compared to the neutral molecule. In alkaline solution, the indole can exist as a dianion:



Depending on the relative acidity of the two acid hydrogen atoms in indole, the two anion forms corresponding to the above ionization will be in equilibrium with each other and with the dianion. The presence of only one peak in the fluorescence spectrum of the indole in alkaline solution does not indicate that only one form is present.

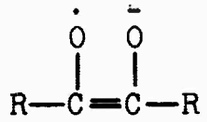
The chemiluminescence spectrum is dissimilar to that of the anion and of unionized indole. There is, however, a close resemblance to the chemiluminescence spectrum of 2,3-dimethylindole. The matching of the two bands indicates similar emittors, which can be identified with the chemiluminescence emission. A distinct difference between this reaction and that of 2,3-dimethylindole

is the absence of a fluorescence peak in the partially oxidized solution which corresponds to the chemiluminescence.

2. Acyloins

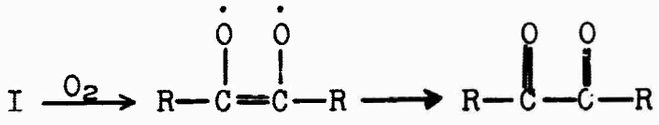
a. Oxidation Mechanism

The acyloins have been subject to considerable study (ref. 8, 9) leading to the identification of the resonance-stabilized aromatic radical anion (I)



(I)

by ESR spectra (ref. 6, 10). This work has recently been extended to the alicyclic (ref. 11) and alkyl (ref. 12) derivatives. The data in Table 3 reveal the decrease of the chemiluminescence intensity with decreasing resonance stabilization of the radical anion (I). This behavior is to be expected if the chemiluminescence is associated with the oxidation of the radical anion. This assumption is supported by the qualitative observation that the luminescence intensity peak occurs with the discharge of the characteristic intense absorption. It therefore becomes plausible that at least some fraction of the excitation energy required for chemiluminescence is derived by the direct oxidative excitation mechanism proposed by Chandross (ref. 13). This process may be written in the conventional structural formulas as



(II) (III)

where the biradical (II) is an excited state of (III).

The chemiluminescence spectrum, on the simplest assumption, should therefore be identical with the luminescence spectrum of photoexcited benzil under the same conditions.

b. Luminescence Spectra

Typical luminescence spectra of benzoin, benzil, and oxidized benzoin in DMSO are given in Figures 5 and 6. Major emission peaks in these uncorrected spectra are seen at 370, 425 and 505 ± 10 mμ.

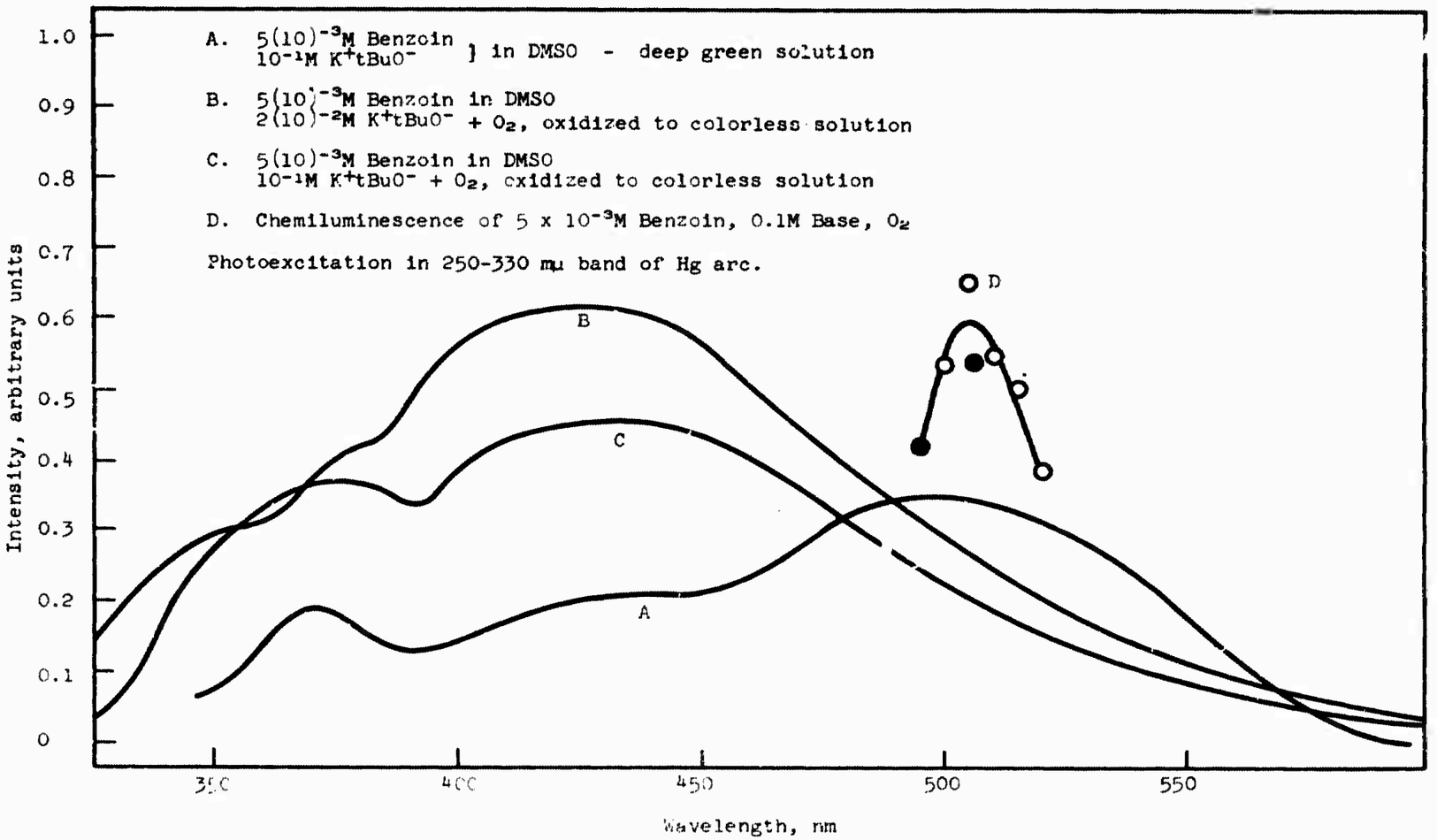


Figure 5. Photoluminescence Spectra of Oxidized Solutions of Benzoin; Chemiluminescence Spectrum of Benzoin Autoxidation

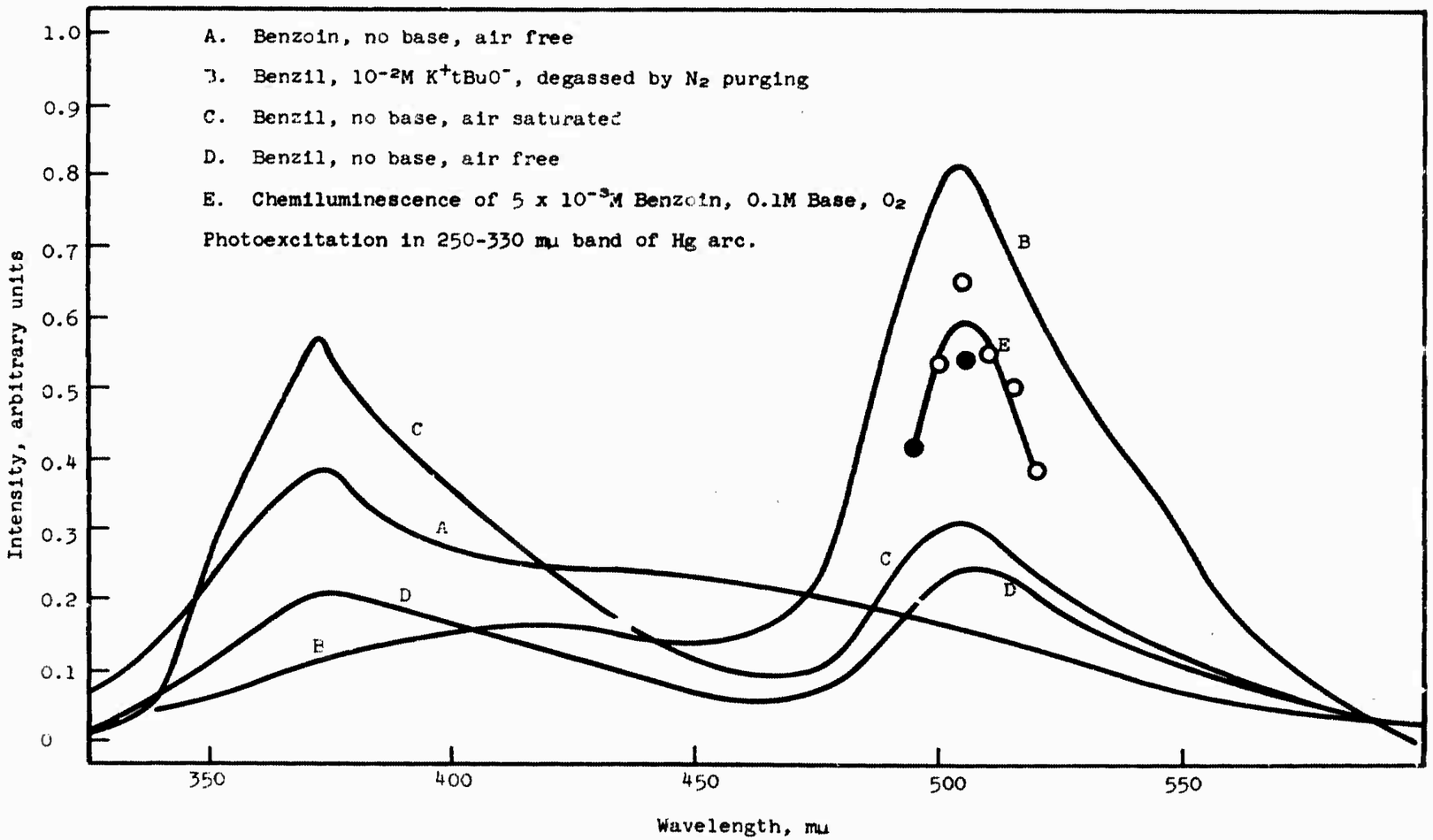


Figure 6. Photoluminescence Spectra of 5 x 10^{-3}M Benzil, 5 x 10^{-3}M Benzoin and Chemiluminescence Spectrum of Benzoin Autoxidation

The salient feature of these spectra is the coincidence between the chemiluminescence emission at 505 mμ and the benzil emission at the same wavelength. Backstrom (ref. 14) has analyzed the luminescence spectra of a number of diketones and has shown that the fluorescence emission of benzil in benzene peaks at 508 mμ. Our measurements of the absorption spectrum of benzil in base-free DMSO confirm the absence of a major solvent shift and lead, therefore, to the assignment of the 505 mμ peak to the singlet transition or fluorescence spectrum of benzil.

With the exception of the identified fluorescence, the spectra are at present not amenable to analysis, since the intensities and peaks observed apparently reflect a rather complex chemistry and are found to be dependent upon reaction variables such as hydroxylic species (OH^-, t-BuOH, and H_2O) and time. Thus, the 370 mμ peak generally observed in both benzil and benzoin is absent in Figure 6B. Deliberate addition of water (1%) has been found to accentuate this peak.

The absence of the 505 mμ benzil fluorescence peak in the oxidized benzoin samples indicates that either a relatively rapid rearrangement occurs or that benzil may be only a minor product of the chemiluminescent reaction.*

The chemiluminescence spectrum observed appears to rule out a major contribution from the phosphorescence, reported by Backstrom to the peak at 565 mμ in oxygen-free benzene. However, this fundamental point will be investigated in some detail.

c. Quenching Behavior

The photochemistry of the triplet states of biacetyl and benzophenone indicate their biradical behavior. In the presence of compounds with labile hydrogen atoms, the excited triplet can abstract the hydrogen to form free radicals. Quenching of the chemiluminescence by hydrogen donating molecules will be investigated. Effects of the addition of compounds such as diphenylamine and t-butyl alcohol to benzoin-base mixtures will also be investigated. We have found that traces of water in DMSO quench the chemiluminescence although the characteristic color changes are still observed as in water-free systems. This suggests that ion radicals are stable in the water-contaminated solvent and that the inhibitory action may involve the quenching of excited benzil.

Other electron acceptors will be investigated in the oxidation reaction of benzil anion donor with the acceptor oxygen molecule.

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* The difficulty of obtaining a stable reproducible spectrum of benzoin has been reported by Bozheval'nov(ref. 15) and Ermolaev (ref. 16).

Nitrobenzene has been reported to be a very efficient electron acceptor from benzil anion. Other compounds that have lower or similar reduction potentials are p-chloronitrobenzene, 9,10-anthraquinone and p-benzoquinone (ref. 17). These molecules should therefore also be good electron acceptors from benzil semiquinone. Electron transfer reactions of this type occur in the absence of oxygen. The use of such acceptors will minimize the quenching of triplet states by high concentrations of paramagnetic oxygen molecules.

IV. FUTURE RESEARCH

A. MAJOR OBJECTIVES

The major objectives for the next quarter are:

(1) Calibration of the spectrometer.

(2) Investigation of the mechanism of benzoin chemiluminescence.

(3) Identification of the radiating species for selected indoles.

(4) Determination of major structural parameters for vinyl and polynuclear aromatic compound chemiluminescence.

(5) Further investigation of solvent, structure, and catalytic effects on selected reactions, including initiation of studies of heterogeneous catalysis.

B. INSTRUMENTATION

The relative spectral response of the photomultiplier will be obtained by substitution of the standard thermopile. The absolute calibration will be determined with the luminol standards recently proposed by Lee and Seliger (ref. 18).

C. BENZOIN LUMINESCENCE

The possible contribution of direct triplet emission to the chemiluminescence of benzoin will be tested by the quenching and sensitization technique of Backstrom. The luminescence will also be determined as a function of concentration to determine whether intermolecular energy transfer excitation is of significance. Flash photolysis excitation of benzil in the same reaction media will be employed to determine the apparent lifetime of any long-lived emittor (ref. 19).

D. INDOLES

The determination of the chemiluminescence and fluorescence spectra of the more efficient indoles will be continued with emphasis upon identification of the emitting species. Selected indoles or reaction products that cannot be purchased will be synthesized. One interesting example is 5-carboxy-3-methylindole which will be used to illustrate the effect of the important 5-substitution upon the chemiluminescence of one of the brightest indoles. As a standard, the chemiluminescence of a zone-refined sample of skatole will be determined.

E. BRIGHTNESS PARAMETERS

Further studies of the effect of solvent medium upon brightness will be conducted, particularly for the brighter indoles. This work will include the effect of rigid exclusion of proton donors, such as t-BuOH, by use of bases such as NaH in DMSO, and additional solvents such as trioctylphosphine oxide plus diluent, and hexamethyl phosphoric triamide. Initial investigations will be begun on heterogeneous autoxidation reactions.

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4. Calculated from data for equilibration with pure O_2.

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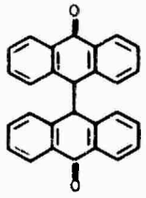
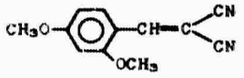
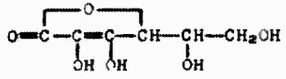
APPENDIX I

AUTOXIDATION REACTIONS

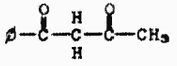
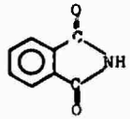
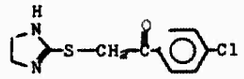
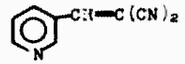
APPENDIX I

AUTOXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to‡ O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
1	10,10'-Bianthrone 	a		$>2 \times 10^{-2}$	1.4×10^{-3}	15 s	green	red	2.5×10^{-3}M (conc. of Bianthrone) $t_{1/2}$ - 35 s
		b		4×10^{-2}	5×10^{-3}	20 s	green	red	
		c	DPA	1×10^{-2}	9×10^{-3}	20 s	green	red	
2	2,4-Dimethoxybenzilidene malononitrile 	a		1.5×10^{-3}	2×10^{-3}	10 s	yellow	clear	Second peak at $t_{1/2}$ = 200 s $I/Io = 2.5 \times 10^{-3}$
		b	DPA	2.4×10^{-3}	3.6×10^{-3}	20 s	yellow	clear	
3	L-Ascorbic acid 	a		6×10^{-4}	3.6×10^{-3}	15 s	yellow	clear	Second peak at $t_{1/2}$ = 95 s $I/Io = 2.4 \times 10^{-3}$
		b	DPA	2.4×10^{-3}	4.4×10^{-3}	15 s	yellow	clear	Second peak at $t_{1/2}$ = 3 m $I/Io = 2 \times 10^{-3}$
4	2,3,4,5-Tetraphenyl pyrrole 	a		2.1×10^{-3}	2.4×10^{-3}	50 s			$t_{1/2}$ = 360 s
		b	DPA	1.2×10^{-2}	3.6×10^{-3}	40 s			$t_{1/2}$ = 270 s
		c	Rubrene	5.4×10^{-3}	1.8×10^{-3}	30 s			$t_{1/2}$ = 510 s

Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
5	1-Phenyl-1,3-butanedione 	a		1.4×10^{-2}	4×10^{-3}	1 m			
		b		1.3×10^{-2}	4×10^{-3}	72 s			
		c	DPA	8×10^{-3}	4×10^{-3}	72 s			
		d	Rubrene	1.5×10^{-2}	2.4×10^{-3}	90 s			
6	Triphenylphosphine 	a		6.6×10^{-2}	4.2×10^{-3}	75 s			
		b	DPA	7.4×10^{-3}	3.6×10^{-3}	65 s			
		c	Rubrene	5×10^{-3}	2×10^{-3}	10 s			
7	Phthalimide 	a		5×10^{-3}	4×10^{-3}	1 m			
		b	DPA	6×10^{-3}	4×10^{-3}	50 s			
8	2-(p-Chlorophenylacylthio)-2-imidazoline 	a		2×10^{-3}	3.6×10^{-3}	200 s			
		b	DPA	2.4×10^{-3}	3.6×10^{-3}	3 m			
9	3-Pyridylmethylene malononitrile 	a		6.4×10^{-3}	3.6×10^{-2}	4 m			
		b	DPA	5×10^{-3}	4.5×10^{-2}	3 m			

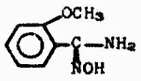
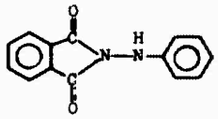
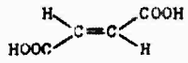
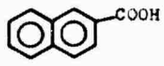
Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to‡ O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
10	Acrylonitrile $H_2C=C=CH-CN$	a		1×10^{-3}	1.2×10^{-2}	28 s	clear	red	$t_{1/2}$ = 75 s
		b	DPA	5×10^{-3}	1.7×10^{-2}	28 s	clear	red	$t_{1/2}$ = 170 s
		c	Rubrene	1.2×10^{-2}	1.9×10^{-2}	25 s	lt orange	dk red	$t_{1/2}$ = 220 s
11	Methylvinylketone $H_2C=CH-C(=O)-CH_3$	a		2.4×10^{-2}	8.2×10^{-2}	10 s	clear	dk red	$t_{1/2}$ = 21 s
		b	DPA	1.8×10^{-2}	6.6×10^{-2}	7 s	clear	dk red	$t_{1/2}$ = 21 s
		c	Rubrene	4.0×10^{-2}	8×10^{-2}	7 s	lt orange	dk red	$t_{1/2}$ = 21 s
12	Anisic acid hydrazide $CH_3O-C_6H_4-C(=O)-NH-NH_2$	a		2×10^{-4}	5×10^{-4}	7 m			
		b	DPA	6×10^{-4}	6×10^{-4}	5 m			
13	Cyanoacetohydrazide $NC-CH_2-C(=O)-NH-NH_2$	a		2×10^{-4}	8×10^{-4}	5 s	clear	red	
		b	DPA	4×10^{-4}	6×10^{-4}	5 s	clear	red	
14	2,5-Diphenyl-1,3,4-oxadiazole $\phi-C_2HN_2O-\phi$			6×10^{-4}	3.6×10^{-4}	40 s			
15	N-Furfurylphthalamic acid $HOOC-C_6H_4-C(=O)-N(H)-C_4H_3O-CHO$	a		2.4×10^{-3}	1.6×10^{-3}	10 s			
		b	DPA	2.2×10^{-3}	2×10^{-3}	10 s			

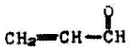
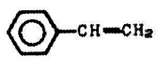
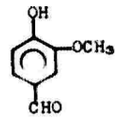
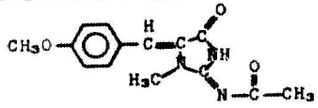
Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initisl† Pulse Ratio	Peak O_2† Current Ratio	Time to‡ O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
16	o-Anisamidoxime 	a b	DPA	5×10^{-4} 5×10^{-4}	6×10^{-4} 4×10^{-4}	5 s 5 s			
17	N-Anilinophthalimide 	a b	DPA	4×10^{-4} 5×10^{-4}	1.2×10^{-3} 6×10^{-4}	6 m 1 m			
18	Fumaric acid 	a b	Rubrene	5×10^{-3} 3.3×10^{-3}	2.4×10^{-3} 7×10^{-4}	6 m 5 s			
19	Isoquinoline 	a b	DPA	1.6×10^{-3} 1.7×10^{-3}	1.7×10^{-3} 2×10^{-3}	10 s 10 s			
20	2-Naphthoic acid 	a b	DPA	2.4×10^{-3} 4×10^{-3}	1.5×10^{-3} 2.4×10^{-3}	5 m 5 s	cl[illegible] clear	red red	Second peak at $t_{1/2} = 8$ m $I/I_0 = 2.4 \times 10^{-3}$

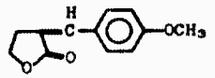
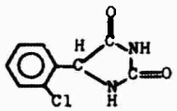
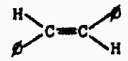
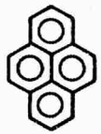
Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to† O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
21	Acrolein (stabilized with hydroquinone 100 ppm) 	a b	DPA	8×10^{-2} 8.6×10^{-2}	7.0×10^{-2} 7.2×10^{-2}	5 s 5 s	clear clear	lt red lt red	$t_{1/2}$ = 11 s $t_{1/2}$ = 10 s
22	Styrene (stabilized with t-butylpyrocatechol) 	a b	DPA	9×10^{-3} 1.8×10^{-3}	5.6×10^{-3} 9×10^{-3}	13 m 19 m			$t_{1/2}$ = 9 m $t_{1/2}$ = 12 m
23	Vanillin 	a b	DPA	1×10^{-3} 9.6×10^{-4}	1.4×10^{-3} 2×10^{-3}	45 s 50 s			
24	N-Methyl-2-pyrrolidone 	a b	DPA	6×10^{-4} 1×10^{-3}	6×10^{-3} 6×10^{-3}	150 s 150 s			
25	1-Methyl-2-acetylimido-5-(4-methoxy-benzilidene)-4-imidazoline 	a		8.4×10^{-4}	1.2×10^{-3}	210 s			

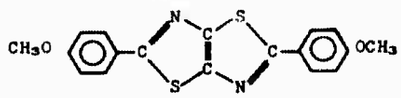
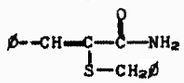
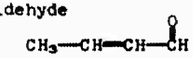
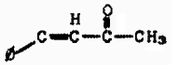
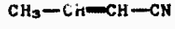
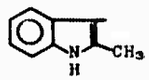
Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to† O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
26	α(2-Hydroxyethyl)-p-methoxycinnamic acid - γ-lactone 	a b	 DPA	9.6×10^{-4} 3×10^{-3}	2.2×10^{-3} 1.8×10^{-3}	7 s 4 m			
27	5-(o-Chlorophenyl)hydantoin 			2×10^{-3}	2.2×10^{-3}	3 m			
28	Trans-stilbene 	a b	 DPA	1×10^{-3} 1.3×10^{-3}	5×10^{-3} 5.2×10^{-3}	3 m 3 m			
29	Pyrene 	a b	 Rubrene	4×10^{-3} 4.4×10^{-3}	4×10^{-3} 1.6×10^{-3}	4 m 5 m			
30	Pyrazine 	a b	 DPA	6×10^{-4} 9×10^{-4}	6.4×10^{-3} 3×10^{-3}	3 m 4 m			

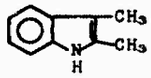
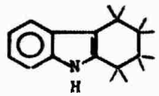
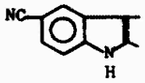
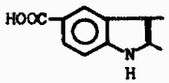
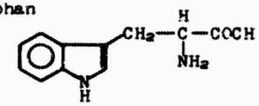
Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to‡ O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
31	2,5-Bis-(4-methoxyphenyl)-thiazolo [5,4-d]thiazole 			1.16×10^{-2}	1.4×10^{-2}	2 m			
32	α-Benzylthiocinnamide 			4×10^{-3}	1.2×10^{-2}	30 s			
33	Crotonaldehyde 			2.6×10^{-2}	2.7×10^{-2}	4 s	clear	dk red	$t_{1/2}$ = 6 s
34	Trans-4-phenyl-3-buten-2-one 	a b	 DPA	8×10^{-3} 1.6×10^{-2}	8×10^{-3} 9×10^{-3}	14 s 7 s	clear clear	dk red dk red	$t_{1/2}$ = 17 s $t_{1/2}$ = 20 s
35	Crotonitrile 			1.0×10^{-2}	1.4×10^{-2}	40 s	clear	dk red	$t_{1/2}$ = 45 s
36	2-Methylindole 			1.8×10^{-2}	6.0×10^{-2}	30 s			$t_{1/2}$ = 55 s

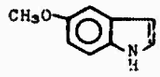
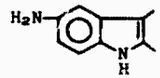
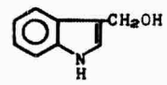
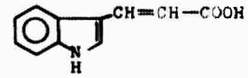
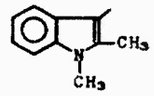
Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to‡ O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
37	2,3-Dimethylindole 			20	60	20 s			$t_{1/2}$ = 60 s
38	1,2,3,4-Tetrahydrocarbazole 			2.1×10^{-2}	2.6×10^{-2}	20 s			$t_{1/2}$ = 50 s
39	5-Cyanoindole 			2.6×10^{-2}	2.6×10^{-2}	2 m			$t_{1/2}$ = 9 h
40	Indole-5-carboxylic acid 			0.2	1.1	3 m			$t_{1/2}$ = 1 h
41	D-Tryptophan 			8.0×10^{-2}	0.86	90 s			$t_{1/2}$ = 8.5 m

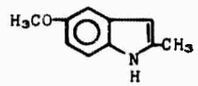
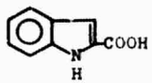
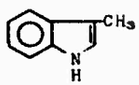
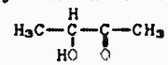
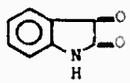
Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to‡ O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
42	5-Methoxyindole 	a b	 DPA	1.1×10^{-2} 1.7×10^{-2}	1.3×10^{-2} 2.6×10^{-2}	2 m 1 m			$t_{1/2}$ = 120 s
43	5-Aminoindol 	a b	 DPA	4×10^{-2} 2×10^{-3}	1.1×10^{-2} 1.4×10^{-2}	6 s 7 s			$t_{1/2}$ = 13 s $t_{1/2}$ = 13 s
44	Indole-3-carbinol 	a b	 DPA	9×10^{-2} 9×10^{-2}	8.6×10^{-2} 6×10^{-2}	21 s 26 s			$t_{1/2}$ = 9 m $t_{1/2}$ = 10 m
45	Indole-3-acrylic acid 	a b	 TP	3×10^{-3} 1.3×10^{-2}	1.1×10^{-2} 1.2×10^{-2}	6 m 330 s			$t_{1/2}$ = 16 m $t_{1/2}$ = 20 m
46	1,2-Dimethylindole 	a b c	 TPB Rubrene	2×10^{-3} 2×10^{-3} 3×10^{-3}	1.2×10^{-2} 1×10^{-2} 4×10^{-3}	4 m 150 s 310 s			$t_{1/2}$ = 4.5 m $t_{1/2}$ = 5 m $t_{1/2}$ = 7 m

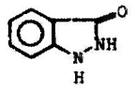
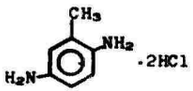
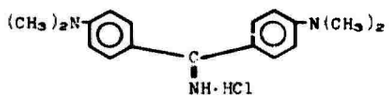
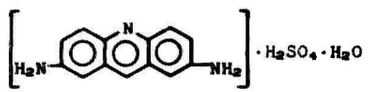
Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to‡ O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
47	5-Methoxy-2-methylindole 	a b	 DPA	7×10^{-3} 8×10^{-3}	1×10^{-2} 8.8×10^{-2}	3 m 3 m			$t_{1/2}$ = 6 m $t_{1/2}$ = 7 m
48	Indole-2-carboxylic acid 			6×10^{-3}	5×10^{-3}	25 s			$t_{1/2}$ = 5 m
49	Skatole (3-Methylindole) 			10	2.4×10^{2}	60 s			K^+tBuO^- conc. 0.067 M, solvent DMF, skatole conc. 5×10^{-3}, $t_{1/2}$ = 210 s
50	3-Hydroxy-2-butanone (Acetoin) 	a b	 DPA	2.2×10^{-3} 2.4×10^{-3}	1.8×10^{-3} 3.3×10^{-3}	4 m 40 s	dk brown dk brown	clear clear	
51	Isatin 	a b	 Rubrene	1.2×10^{-2} 1.4×10^{-2}	1×10^{-2} 1.1×10^{-2}	10 s 10 s	clear	orange	

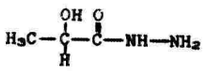
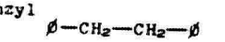
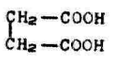
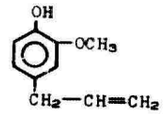
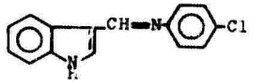
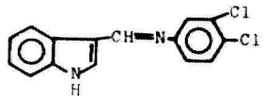
Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to‡ O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
52	3-Indazolinone 	a		6×10^{-2}	1.6×10^{-3}	2 m			
		b	DPA	1.4×10^{-1}	8×10^{-3}	3 m			
		c	Rubrene	1.2×10^{-1}	3.3×10^{-3}	45 s			
53	2,5-Toluenediaminedihydrochloride 	a		4×10^{-4}	2.2×10^{-4}	30 s		deep red	
		b	Rubrene	1.4×10^{-1}	2.2×10^{-4}	5 s		deep red	
54	Auramine O 	a		8×10^{-3}	7.6×10^{-3}	20 s		brownish-yellow	
		b	Rubrene	8×10^{-3}	5×10^{-3}	25 s		brownish-orange	
		c	DPA	5×10^{-3}	2.8×10^{-3}	270 s		brownish-yellow	
55	Acriflavinhydrochloride 	a		5×10^{-3}	3.1×10^{-4}	390 s			
		b	DPA	4.4×10^{-3}	7×10^{-4}	5 s			
		c	Rubrene	1×10^{-3}	2.5×10^{-4}	210 s			
56	3,6-Diaminoacridinehemisulfate-hemihydrate 	a		2×10^{-3}	5×10^{-4}	15 s		deep red	
		b	Rubrene	$1.x 10^{-3}$	2×10^{-4}	10 s		deep red	
		c	DPA	5×10^{-3}	2.4×10^{-4}	10 s		deep red	

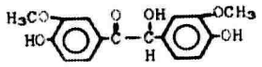
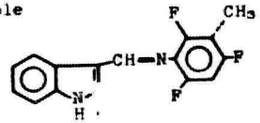
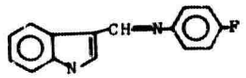
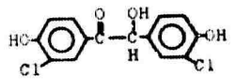
Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to‡ O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
57	Lactic acid hydrazide 	a b c	DPA Rubrene	2.4×10^{-3} 7×10^{-3} 1.1×10^{-2}	2×10^{-3} 1.3×10^{-3} 1.6×10^{-3}	5 s 150 s 5 s			
58	Bibenzyl 	a b	Rubrene	9×10^{-3} 4.2×10^{-3}	1.8×10^{-3} 1.2×10^{-3}	5 s 5 s			
59	Succinic acid 	a b	DPA	5×10^{-3} 5×10^{-3}	1.5×10^{-3} 1.4×10^{-3}	5 s 5 s			
60	Acridine 	a b c	DPA Rubrene	0.4 0.4 0.3	5.0 5.0 2.0	15 s 30 s 5 s		red red red	
61	Eugenol 	a b c	DPA Rubrene	2×10^{-2} 1.8×10^{-2} 2.6×10^{-2}	1.4×10^{-2} 1.3×10^{-2} 4×10^{-3}	45 s 3 m 1 m			
62	3-N-Para(chlorophenyl)formidoyl-indole 	a b	DPA	1.7×10^{-2} 4.4×10^{-2}	1.3×10^{-2} 1.3×10^{-2}	5 s 5 s			$t_{1/2} = 5$ s
63	N-3,4-Dichlorophenylformidoylindole 	a b c	DPA Rubrene	1.3×10^{-2} 1.4×10^{-2} 6×10^{-3}	3.7×10^{-3} 2.8×10^{-3} 4×10^{-3}	2 m 210 s 4 m			

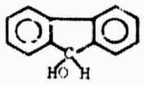
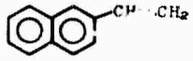
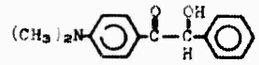
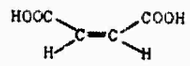
Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to‡ O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
64	4,4'-Dihydroxy-3,3'-dimethoxybenzoin 	a b	Rubrene	6×10^{-2} 7×10^{-3}	3.4×10^{-3} 4×10^{-3}	25 s 5 s	colorless solution colorless solution		
65	3-N-Metatrifluoromethylformidoyl-indole 	a b c	DPA Rubrene	8×10^{-3} 5×10^{-3} 5×10^{-3}	7×10^{-3} 2×10^{-3} 3×10^{-3}	7 m 4 m 5 m			
66	3-N-Parafluorophenylformidoylindole 	a b	Rubrene	6×10^{-3} 3×10^{-3}	5×10^{-3} 1.5×10^{-3}	4 m 270 s			
67	3,3'-Dichloro-4,4'-dihydroxybenzoin 	a b c	DPA Rubrene	3×10^{-2} 2.7×10^{-3} 7×10^{-3}	5×10^{-3} 5×10^{-3} 2.4×10^{-3}	5 s 3 s 5 s	colorless solution		
68	Acrylic acid (stabilized with p-methoxyphenol) $H_2C{=}CH{-}COOH$	a b	DPA	6×10^{-4} 2×10^{-4}	2.5×10^{-3} 3.2×10^{-3}	150 s 210 s			Did not turn dark $t_{1/2}$ = 5 m Did not turn dark $t_{1/2}$ = 3.5 m

Notes are at the end of this table.

APPENDIX I (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial† Pulse Ratio	Peak O_2† Current Ratio	Time to‡ O_2 Peak	Appearance Before O_2	Appearance After O_2	Comments
69	9-Hydroxyfluorene 	a b	DPA	2×10^{-3} 2×10^{-3}	9.2×10^{-2} 6.4×10^{-2}	35 s 20 s			$t_{1/2}$ = 30 s $t_{1/2}$ = 40 s
70	2-Vinylnaphthalene 	a b	DPA	1.2×10^{-2} 1.2×10^{-2}	2×10^{-3} 3.6×10^{-3}	5 m 150 s			$t_{1/2}$ = 5 m $t_{1/2}$ = 7 m
711	4-Dimethylaminobenzoin 			2×10^{-3}	4×10^{-1}	23 s	deep purple	clear	Same color sequence as benzoin $t_{1/2}$ = 7 s
72	Maleic acid 	a b	DPA	2×10^{-3} 1×10^{-3}	2.4×10^{-3} 9×10^{-4}	5 m 4 m			

NOTES: *Abbreviations
DPA - 9,10-Diphenylanthracene
TP - p-Terphenyl
TPB - 1,1,4,4-Tetraphenylbutadiene

†Ratio of photometer current produced by standard source

‡s = second
m = minute
h = hour

REACTION CONDITIONS: All compounds 5×10^{-3}M in 0.1M K^+tBuO^- in DMSO; sensitizers 10^{-4} unless other ise noted.

APPENDIX II

TOXICITY OF SELECTED COMPOUNDS

APPENDIX II

TOXICITY OF SELECTED COMPOUNDS

No.	Compound	Toxicology	Toxic Hazard Rating
1	Acridine	Strongly irritating to skin and mucous membranes; causes sneezing upon inhaling.	
2.	Acrolein	Strong irritation of skin and exposed mucous; habitual exposure seems to lead to some tolerance; no other chronic ill effects have been reported.	
3	Acrylonitrile	Weakness, light-headedness, headache, nausea, sneezing, abdominal pain, vomiting, loss of consciousness, cessation of respiration (asphyxia) and death.	Maximum allowable concentration is 20 ppm.
4	Benzoin		Acute local: irritant 1 allergen 1 ingestion 1 Acute systemic U Chronic local: allergen 1 Chronic systemic: U
5	Crotonaldehyde	A lachrymating material which is very dangerous to the eyes.	Acute local: irritant 3 allergen 2 ingestion 3 inhalation 3

APPENDIX II (Continued)

No.	Compound	Toxicology	Toxic Hazard Rating
	Crotonaldehyde (continued)		Acute systemic: U Chronic local: allergen 2 Chronic systemic: U
6	Indole		Lethal dosage i.v. in dogs 60 mg/kg
7	Methyl vinyl ketone	Skin irritant and lachrymator.	
8	Skatole		Minimum lethal dosage s.c. in frogs 1.0 g/kg.
9	L-Tryptophan	Medical use: nutrient. Recommended intake for normal adult male 0.5 g/day. Tryptophan and proteins containing Tryptophan are effective in preventing and treating pellagra.	

Note: Toxic rating code: 0 = none
1 = slight
2 = moderate
3 = high
U = unknown

References: 1. "Dangerous Properties of Industrial Materials", Sax, Newton Irving, Reinhold Pub. Co., New York, 1957.

2. "Merck Index of Chemicals and Drugs", Paul G. Stecker (Ed), 7th Ed., Merck Chem. Co., Rahway, New Jersey, 1960.